

Charge ordering signatures in the optical properties of β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$

C. Presura, M. Popinciuc, P. H. M. van Loosdrecht, D. van der Marel, M. Mostovoy,
*Material Science Center, University of Groningen,
 Nijenborgh 4, 9747 AG Groningen, The Netherlands*

T. Yamauchi, Y. Ueda
*Institute for Solid State Physics, University of Tokyo, Japan
 (Dated: February 1, 2008)*

Temperature dependent optical spectra are reported for β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$. The sodium ordering transition at $T_{\text{Na}} = 240$ K, and in particular the charge ordering transition at $T_{\text{MI}} = 136$ K strongly influence the optical spectra. The metal-insulator transition at T_{MI} leads to the opening of a pseudogap ($\hbar\omega = 1700 \text{ cm}^{-1}$), and to the appearance of a large number of optical phonons. These observations, and the presence of a mid-infrared band (typical for low dimensional metals) strongly suggests that the charge carriers in β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ are small polarons.

Low dimensional metals feature a variety of MI transitions resulting from electron-phonon or electron-electron interactions. In charge density wave systems, like NbSe_3 [1] and $\text{K}_{0.3}\text{MoO}_3$ [2, 3], a MI transition is induced by a strong electron-phonon coupling (Peierls state). In Fe_3O_4 and Ti_4O_7 [4], which are polaronic materials, a MI transition is induced by small polaron ordering (Verwey state). Finally, in systems lacking sufficiently strong electron-phonon interaction, such as for instance $(\text{Me}_2 - \text{DCNQI})_2\text{Li}_{1-x}\text{Cu}_x$ [5, 6], a MI transition may occur due to charge ordering resulting from electronic coulomb interactions (Wigner crystal). Materials of which the properties are dominated by electron-phonon interaction often show the appearance in the insulating state of a large number of phonons in the infrared spectrum along the chain direction. This phenomena, discussed by Rice [7] for the 1D organic peierls compound $\text{TEA}(\text{TCNQ})_2$, has been found in several materials [1, 2, 3, 8], including those showing a Verwey transition. One of the intriguing features of all these materials is that they show a so called mid-infrared band in the optical spectra. It has been argued that for Fe_3O_4 [9] and many other materials [10] the mid-infrared band can be understood as a polaronic response. However, also materials where Hubbard physics dominates may show a relatively strong mid-infrared band resulting from intra-band transitions [5, 6, 11, 12].

The recent discovery [13] of a clear metal-insulator transition (MIT) in the vanadium bronze β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ has sparked a revival of interest in this quasi one-dimensional (1D) metallic system. The room temperature crystal structure [14] of β - $\text{Na}_x\text{V}_2\text{O}_5$ presents three crystallographically distinct Vanadium sites, labelled V_1 , V_2 and V_3 . The Na atoms occupy lattice positions which can be represented as a ladder along the b axis (the chain direction). For $x = 1/3$ only 50 % of these lattice sites is occupied, each rung hosting one Na atom randomly distributed between the left and right hand side of the ladder. Each Na-atom donates one electron to the otherwise empty vanadium d bands. It is believed [15] that these

electrons are shared among the three V chains above the metal-insulator transition $T_{\text{MI}} = 136$ K, and that they condense on the V_1 zig-zag chain or the V_2 ladder below T_{MI} . The metallic nature is rapidly lost for small deviations from $x = 0.33$ [13]. The presence of metallic behavior for only a sharply defined charge carrier concentration is different from conventional MIT in 2 or 3 dimensions, where the metallic phase occurs in a broad range of carrier densities above the critical value. This unusual doping dependence probably results from the potential created by the neighboring Na atoms. Doping away from $x = 1/3$ creates empty or fully occupied rungs on the Na ladder leading to large potential variations at the vanadium sites, and thus a decreased conductivity and eventually a localization of the charges.

β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ exhibits three phase transitions as a function of temperature: A sodium ordering transition at $T_{\text{Na}} \cong 240$ K accompanied by a doubling of the unit cell along b , a MI transition at $T_{\text{MI}} \cong 136$ K showing an additional tripling of the unit cell [16], and finally an anti-ferromagnetic transition at $T_{\text{CAF}} \cong 22$ K [13, 17, 18]. The nature of the MI transition in β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ is presently unclear. There has been a suggestion that it results from bi -polaronic ordering [19, 20]. But since the temperature dependent magnetic susceptibility [13] shows that the spins of the charge carriers remain unpaired in the insulating state this is an unlikely scenario. Another suggestion is that the charge ordering transition is a Peierls transition [21]. This, however, is based on the assumption that β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ becomes a quarter filled system below T_{MI} , which is contradicted by experiments showing a tripling of the unit cell along the b -direction. As is clear from the above, the origin of the MI transition as well as the nature of the charge carriers and the relevance of electron-phonon interactions remain open problems in β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$. This motivated the present study on the temperature dependent optical conductivity of β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$.

Single crystals have been prepared as described in [13]. We measured the reflectivity in the range 20 - 6000 cm^{-1}

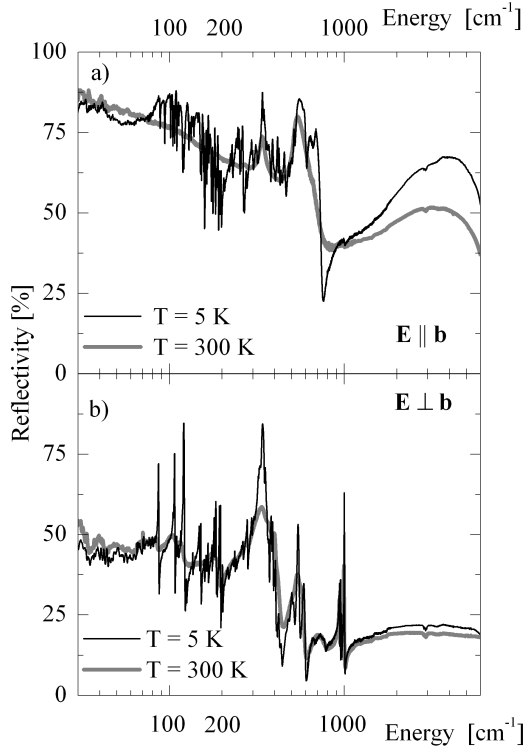


FIG. 1: Reflectivity spectra of β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ for $\mathbf{E} \parallel \mathbf{b}$ (a) and $\mathbf{E} \perp \mathbf{b}$ (b).

as a function of temperature with a polarizations both parallel and perpendicular to the b -direction (*i.e.* parallel to the conducting chains). Figure 1 shows the reflectivity spectra for some selected temperatures. In addition, we used spectroscopic ellipsometry to determine the dielectric function from 6000 to 36000 cm^{-1} at room temperature. The optical conductivity was obtained by combining the reflectivity and ellipsometry data and performing a Kramers-Kronig analysis (see Fig. 2). The one-dimensional nature of β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ is clearly reflected in the room temperature spectra. The b -direction shows a finite low frequency conductivity extrapolating to 200 Ωcm^{-1} at zero frequency. This value is somewhat better than the DC value of 100 Ωcm^{-1} measured previously [13]. In contrast, the conductivity in the perpendicular direction shows a typical insulating behavior in that the conductivity extrapolates to zero for zero frequency. The other features observed in the spectra are several relatively sharp phonon lines, and more importantly a relatively strong mid-infrared band along the chain direction. The sodium ordering and in particular the MI transitions strongly influence the optical spectra. At the sodium ordering transition a small number of new phonon modes appear in the $\mathbf{E} \perp \mathbf{b}$ polarization. Their intensities have a slow temperature dependence reminiscent of an order/disorder transition and in good agreement with the temperature evolution of the satellites observed in X-ray

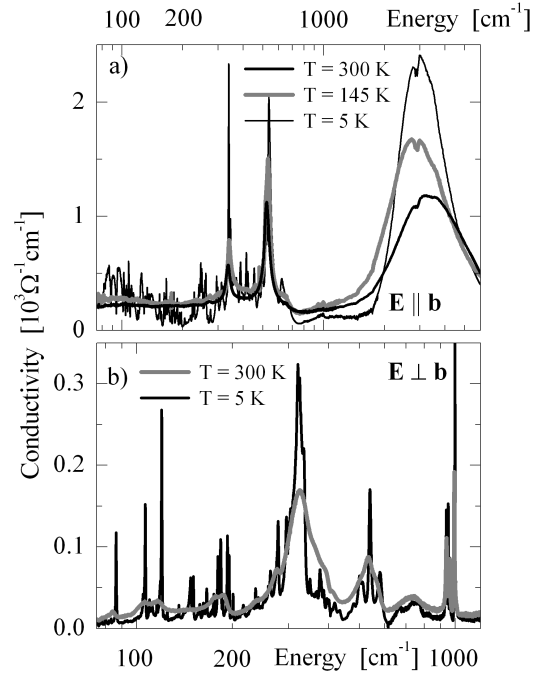


FIG. 2: The optical conductivity for $\mathbf{E} \parallel \mathbf{b}$ (a) and $\mathbf{E} \perp \mathbf{b}$ (b). The two small dips on the 3000 cm^{-1} peak are due to water absorptions. Note the different energy scales in panel (a) and (b).

diffraction experiments [22]. This is exemplified for a mode appearing at 990 cm^{-1} in figure 3b. More spectacularly, the MI transition results in the appearance of a large number of sharp phonon lines (more than 60 for the polarization along the b -direction, see figure 3a for a detailed view). This evidences the presence of strong electron-phonon coupling in β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$. Another indication for important electron-phonon interactions is the observation of strongly distorted phonon line shapes in the low frequency part ($< 150 \text{ cm}^{-1}$) of the conductivity along the b -direction (figure 2a). The temperature dependence of the intensity of the phonons appearing in the insulating state exhibits a clear 2nd-order nature (see figure 3b, 950 cm^{-1} mode). A second change in the optical conductivity below the MI transition is the opening of a pseudo-gap below 1700 cm^{-1} in the b -direction (see figures 2a and 3c). This opening of the pseudogap, apparent as a clear decrease in the background intensity below T_{MI} , is somewhat obscured by the appearance of the many phonon peaks in the insulating phase.

An important clue for the interpretation of the optical spectra below 8000 cm^{-1} is provided by the observation, that while a gap opens in the optical spectrum and the DC-resistivity below 136 K, the magnetic susceptibility is almost unaffected by the metal-insulator transition. If the gap were of the garden variety like in silicon, the spin-fluctuations would become strongly suppressed below the same temperature where the optical conductivity

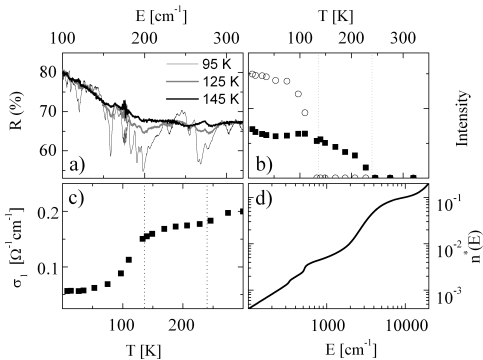


FIG. 3: a) detail of the reflectivity spectrum for $\mathbf{E} \parallel \mathbf{b}$ for $T=95, 125$, and 145 K. b) Temperature dependence of the intensity of two phonons appearing in the $\mathbf{E} \perp \mathbf{b}$ spectra at 990 cm^{-1} (full symbols) and 950 cm^{-1} (empty symbols). c) Temperature dependence of the $\mathbf{E} \parallel \mathbf{b}$ optical conductivity for $E = 750 \text{ cm}^{-1}$. d) Effective number of electrons calculated from the $\mathbf{E} \parallel \mathbf{b}$ optical conductivity using equation 1.

ity becomes gapped. However, in $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ there is no formation of a spin-gap when charge transport gets suppressed below 136 K [13]. This aspect of the data reflects the presence of strong on-site Hubbard-type repulsions between the charge carriers, which in one-dimension causes the electrons to behave like spinless fermions, and it may thus be an experimental candidate for the material which can reproduce the main theoretical expectations of the partly occupied Hubbard chain: spin charge separation, and fractionalization of the charge [23]. The relative independence of the spin and charge channels has been noticed before for the Bechgaard salts [24], the presence of a pseudogap in the optical excitations being opposed to the absence of a gap for spin excitations. Another important clue is provided by considering the optical response of the charge carriers: In a previous study[25], a minimum in the $E \parallel b$ reflectivity at 7200 cm^{-1} has been attributed to a plasma edge. We can see from Fig. 2a, that the main contribution to the oscillator strength associated with this plasma minimum arises from the prominent mid-infrared band centered at 3000 cm^{-1} . By integrating the optical conductivity, and adopting the bare mass m_e for the electrons, we calculated the effective number of electrons displayed in the figure 3d) using

$$8 \int_0^\omega \sigma_1(\omega') d\omega' = n^*(\omega) \frac{4\pi n_V e^2}{m_e}. \quad (1)$$

The integrated spectral weight of the mid-infrared feature corresponds to $n^*(10000 \text{ cm}^{-1}) \simeq 0.10$ electrons per V atom, which is rather close to the nominal chemical doping of $n = 0.166$ electrons per V atom. (The difference can be easily understood from the fact that in these transition metal oxides the effective mass of the electrons is about $2m_e$.) The high oscillator strength of the mid-infrared peak as shown by the value of n^* shows that it arises from the doped charge carriers. In con-

trast the spectral weight of the low frequency part up to 1500 cm^{-1} is about 10% of the total mid-infrared feature (see inset Fig.2c). Finally, the relative intensity of the low frequency spectral weight (in comparison to the 3000 cm^{-1} peak) is almost independent of temperature above T_{MI} .

From studies of the Hubbard model in one dimension we know, that part of the intra-band spectral weight shows up as a band of mid-infrared excitations. However, these studies have also demonstrated, that for doping far away from half-filling of the Hubbard band the intensity of the mid-infrared band is less than 20 % of Drude spectral weight[11, 12]. This rules out an interpretation of the mid-infrared peak in $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ in terms of a pure Hubbard model. At the same time we underscore the crucial role of Hubbard-type correlations for the independence of the spin response from the charge-gap in this material.

The most trivial explanation of the 3000 cm^{-1} peak would be that it is a direct transition between bands which are formed as a result of the Umklapp-potential of the Na-superlattice below 240 K . However, the potential landscape caused by the Na ions becomes randomly ordered above 240 K . Although even a random potential would give rise to a mid-infrared peak, the position of the mid-infrared peak would become strongly temperature dependent in such a scenario, in contrast to our experimental observations.

The remaining candidate for the mid-infrared band is to assume that the charge carriers are small polarons. Derived basically from the Frank-Condon model, the small polaron peak [10] can be viewed classically as an instantaneous transition from a localized state to a neighboring localized state in a rigid ionic environment. The environment responds to the new electronic configuration by emitting a wave package of multi-phonon oscillations, the envelope of which corresponds to the line shape of a polaron. It acquires not only a peak at several times the frequency of phonons, but also a finite conductivity at low frequencies. The small polaron optical line shape, being influenced by the movement of ions, depends strongly on temperature [10]. This is indeed what we observe for the mid-infrared feature in its high frequency part (see Fig. 2a).

The low frequency part is unchanged down to the $T_{\text{MI}} = 136 \text{ K}$, in opposition to what is expected[10] and measured[26] for the small polarons. This unexpected behavior may have a connection to the disorder potential created by the Na atoms, which could smear out the influence of the temperature at low frequencies. If so, it would suggest that some disorder in the Na positions exists even below T_{Na} , in other words that the ordering of the Na atoms takes place gradually. This is confirmed by the measured intensity of the 990 cm^{-1} phonon which gradually develops in the insulating direction below T_{Na} , being fully developed at T_{MI} (see figure 3b). They both

suggest that the MIT takes place at a temperature where the Na atoms are fully ordered. This strengthens the argument that the Na potential influences strongly the movement of the electrons on the V chains.

To summarize the interpretation of all optical features: Both the mid-infrared peak at 3000 cm^{-1} , and the observation of strong electron-phonon coupling support the picture that the charge carriers in $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ should be regarded as small polarons. The strong Hubbard-type interactions are responsible for the observed independent behavior of the spin- and charge channels at the metal-insulator phase transition. Below the phase transition the insulating state is a charge ordered phase. Future experiments will have to establish the detailed nature of the charge ordered state. Although in a way a regular array of polarons also represents a CDW, a distinguishing feature in this case, is that in an ordinary CDW the spin- and charge sectors should be gapped simultaneously, which clearly does not happen in $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ at 136 K, where the spin orders at a still lower temperature. The nature of the crystallographic phase transition at 136 K (*i.e.* the tripling of the unit cell along the chains) suggests, that below 136 K the charges have become ordered with a commensuration of order 3 on the three different types of V-chains and ladders in the unit cell. This would imply that the doped charges are either distributed equally over all V-atoms or in a $2/3\text{-}1/3$ ratio over the V_1 and V_2 atoms, resulting in a high degree of dilution. This a favorable condition for the formation of small polarons, consistent with the above interpretation of the spectra.

This work was supported by the Dutch Foundation for Fundamental Research on Matter (FOM) and by INTAS (99-155). We greatly acknowledge A.T. Filip for the polarized microscopy checks and G. Maris and T. T. M. Palstra for fruitful discussions.

[1] W.A.Challenor and P.L.Richards, Solid State Comm. **52**, 117 (1984).

[2] G.Travaglini and P.Wachter, Phys. Rev. B **30**, 1971 (1984).
 [3] L.Degiorgi and G.Gruner, Phys. Rev. B **44**, 7820 (1991).
 [4] N. Mott, *Metal-insulator transitions* (Taylor and Francis, London, 1974).
 [5] T.Yamamoto, H.Tajima, J. Yamaura, S.Aonuma, and R.Kato, J. Phys. Soc. Jpn. **68**, 1384 (1999).
 [6] H. Tajima, Solid State Comm. **113**, 279 (2000).
 [7] M.J.Rice, L.Pietronero, and P.Bruesch, Solid State Comm. **21**, 757 (1977).
 [8] L. Degiorgi, P. Wachter, and C.Schlenker, Physica B **164**, 305 (1990).
 [9] L.Degiorgi, P.Wachter, and D.Ihle, Phys. Rev. B **35**, 9259 (1987).
 [10] D. Emin, Phys. Rev. B **48**, 13691 (1993).
 [11] R.M.Fye, M.J.Martins, D.J.Scalapino, J.Wagner, and W.Hanke, Phys. Rev. B **45**, 7311 (1992).
 [12] H.J.Schulz, Phys. Rev. Lett. **64**, 2831 (1990).
 [13] H. Yamada and Y. Ueda, J. Phys. Soc. Jpn. **68**, 2735 (1999).
 [14] A. Wadsley, Acta Cryst. **8**, 695 (1955).
 [15] M.Itoh, N.Akimoto, H.Yamada, M.Isobe, and Y.Ueda, J. Phys. Soc. Jpn. **Suppl.B 69**, 155 (2000).
 [16] J.Yamaura, M.Isobe, H.Yamada, T.Yamauchi, and Y.Ueda, J. Phys. Chem. Solids **63**, 957 (2002).
 [17] A. N. Vasil'ev, V.I. Marchenko, A. I. Smirnov, S. S. Sosin, H. Yamada, and Y. Ueda, Phys. Rev. B **64**, 174403 (2001).
 [18] Y.Ueda, H.Yamada, M.Isobe, and T.Yamauchi, J.Alloys and Compounds **317-318**, 109 (2001).
 [19] H. Kobayashi, Bull. Chem. Soc. Japan **52**, 1315 (1979).
 [20] B.K. Chakraverty, M.J. Sienko, and J. Bonnerot, Phys. Rev. B **17**, 3781 (1978).
 [21] G. Obermeier, D. Ciesla, S. Klimm, and S. Horn, cond-mat/0203234.
 [22] Y. Kanai, S. Kagoshima, and H. Nagasawa, J. Phys. Soc. Jpn. **51**, 697 (1987).
 [23] S.C. Zhang, S. Kivelson, and A.S. Goldhaber, Phys. Rev. Lett. **58**, 2134 (1987).
 [24] V.Vescoli, L.Degiorgi, W.Henderson, G.Gruner, K.P.Starkey, and L.K.Montgomery, Science **281**, 1181 (1998).
 [25] D. Kaplan and A. Zylbersztejn, J. de Physique **37**, L (1976).
 [26] S.K.Park, T.Ishikawa, and Y.Tokura, Phys. Rev. B **58**, 3717 (1998).